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(54) AEROSOL CAN

(57)Abstract:
PURPOSE: To permit the production of an aerosol can resistant to a compound difficultly usable as the aerosol product by using the coating film consisting chiefly of polyvinylidenefluoride as a covering for the inner wall of the aerosol can.
CONSTITUTION: In an aerosol can to be filled with aerosol compositions difficultly usable as an aerosol article, a coating film consisting chiefly of polyvinylidenefluoride is used as a covering for the inner wall of a can such as made of iron, tinplate and aluminum. Also, the valve covered with the same coating film is used. The use of such coating film brings about resistance particularly to a polar medium liquid mixture containing the compound and oxidizing agent capable of giving off acid and/or oxygen. Therefore, the aerosol article can be produced even from the compound which has hitherto been difficultly usable to make this process technically feasible.

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Specification

1. Title of the invention
   Aerosol cans.

2. Scope of Claim
   1 An aerosol can made of a metal container, the inner wall of which is coated with a film consisting chiefly of polyvinyldenefluoride.
   2 An aerosol can defined under Claim 1, equipped with the valve, the inner wall of which is coated with the a film consisting chiefly of polyvinyldenefluoride.
   3 An aerosol article of an aerosol can defined under Claim 1 or 2 filled with an aerosol composition made from a spraying agent and a liquid medium, which contains a polar medium solution, dissolving an acid

and/or a compound possibly generating an acid, and an oxidizing agent.

3. Detailed description of the invention

[Industrial application field]

The present invention is related to aerosol cans, which can fill aerosol compositions, so far difficult to be used for aerosol articles.

[Conventional technology and problems]

Aerosol cans used for aerosol articles are filled with many chemicals. Their inner walls are coated with resin to give the chemical resistance to the metal cans. Epoxy resins are being used as such coatings due to the adhesion, anti-corrosive properties and processability. However, the epoxy resin coatings are problematic in view of the anti-corrosive properties, which largely restricts the recipe formation possibilities, when formulating aerosol preparations of medical products, over-the-counter drugs, hair spray, etc., so far resulting in production of less effective aerosol products.

And there have been no aerosol cans resistant to polar media mixtures, which contain severely corrosive acids or compounds capable of generating acids, and oxidizing agents. It has therefore been difficult to prepare aerosol articles of such preparations.

[Process to solve the problems]

The present invention freed from the aforementioned problems can be characterized in short as follows: For the inner wall of the aerosol cans a coating film consisting chiefly of polyvinyldenefluoride (hereafter described as PVdF) is to be adopted.

[Function and examples]

The coating preparations to form the film consisting chiefly of PVdF under the present invention (hereafter described as PVdF-film) are preferably prepared by dissolving or dispersing in a solvent 100 PbW (Parts by Weight: The same shall apply hereinafter.) of PVdF, 1-100 PbW of a binder resin, if necessary up to 40 PbW of ordinary coating additives such as pigments, fillers, dyestuffs, lubricants.

PVdF may be a homopolymer of vinylidenefluoride (VdF) or a copolymer with other monomers. In the case of the copolymers, the content of VdF should at least be 75% (wt %: The same shall apply hereinafter.) to maintain the chemical resistance. As to the monomers capable of being co-polymerized, e.g. ethylene, styrene, propylene, isobutene, vinyl chloride, vinylidene chloride, vinyl fluoride, chlorotrifluoroethylene, tetrafluoroethylene, trifluoropropylene, hexafluoropropylene, hexafluoroisobutylene, vinyl acetate, vinyl propionate, butyl butylate, acrylic acid, methacrylic acid, methyl acrylate, methyl methacrylate, fluoroalkyl acrylate, fluoroalkyl methacrylate, glycidyl methacrylate, allyl alcohol, butyl-vinyl ether, ethyl-vinyl ether, hydroxy-butyl-vinyl ether, maleic

anhydride, vinyl-methoxy silane, etc. can be referred to. PVdF can be prepared by the well-known methods such as the ones described in the Japanese Patent Publications Sho: 46-9476, -26820, -21214, 47-39592, 58-34484.

As for binder resins, thermosetting resins or heat resistant resins are desirable. The binder resins are blended to improve the adhesion of PVdF-film. Their mixing ratio against 100 PbW of PVdF is 1-100 PbW, preferably 5-70 PbW. Too small quantities do not improve the adhesion, and too large amounts damage the properties of PVdF, such as the chemical resistance. As to the concrete examples of the binder resins, e.g. epoxy resin, phenol resin, amino resin, alkyd resin, amide-imide resin, polyparabanic acid, glycidyl group containing copolymer, hydroxyl group containing copolymer, carboxyl group containing copolymer, polyethersulfone, polyether ether ketone, polyimide, polysulfone, polyphenylenesulfide, aromatic polyamide, silicone resin, polyester, etc. can be cited. In the case of the resins poor in the compatibility with PVdF, a suitable amount of an acrylic acid can be added, which has a functional group, such as glycidyl group, carbonyl group, isocyanate group, phosphono group, phosphinico group, amino group, etc.

As to the solvents, ketones, esters, ethers, amides, carbonates, nitriles, phosphates can be referred to. As to the concrete examples, e.g. methyl ethyl ketone, methyl isobutyl ketone, ethyl acetate, N-methyl pyrrolidone, cyclohexanone, Methyl Cellosolve Acetate, isophorone, methyl isoamyl ketone, γ-butyrolactone, Cellosolve Acetate, propylene carbonate, diisobutyl ketone, carbitol acetate, dimethyl phthalate, dimethyl acetamide, dimethyl formamide, trimethyl phosphate, diacetone alcohol, dibutyl phthalate, dimethyl carbitol, tetramethyl urea, acetylacetone, acetophenone, Butyl Cellosolve, acetone, Cellosolve, dioxane, acetonitrile, triethyl phosphate, benzonitrile, triphenyl phosphate, etc. can be cited.

The coating preparations can be prepared by the well-known mixing procedures, such as ball-mill, sand-mill, paint-mill, homodisper(ser), homogenizer, etc. of the aforementioned compositions. The suitable temperature for mixing is below 50 °C. The quantity of the solvent differs depending on the coating method. However, it is usually 50-1000 PbW; a quantity to adjust the viscosity of the preparation to 1-500 cP is desirable.

In order to form the coating film, the following methods are referred to: The inner wall of the metal containers formed in the fixed size of the aerosol cans is coated with the coating film preparation by means of spraying, roller coating, knife coating, curtain flow coating, dipping, etc., then baked at about 80-350 °C, preferably at about 150-330 °C. The thickness of the film is usually 1-50 μm, preferably 5-30 μm. A too thick film causes the coat peeling, foaming during the baking, the coat peeling and cracking during the post processing. When too thin, the corrosion resistance is not sufficient, causing pinholes.

The materials of the metal containers are adopted from the metals used for the ordinary aerosol cans, such as iron, blik, aluminum, stainless steel, tin plate (surface treated steel sheet), etc.

And further, other parts coming in contact with the aerosol preparations, e.g. valves made from the aforementioned metals, copper alloy, tin alloy should also better be coated with the similar PVdF-film.

The aerosol cans of the present invention have the resistance not only to conventional aerosol preparations but also, particularly, to polar medium mixed solutions, which contain acids and/or compounds possibly generating acids, and oxidizing agents, so far difficult to be formulated as aerosol preparations. As the acids and/or the compounds possibly generating acids, carboxyl group containing compounds, ester group containing compounds, sulfonic acid group containing compounds, sulfonyl group containing compounds, organic acid salts, inorganic acids, inorganic acid salts, quaternary ammonium salts, etc., concretely e.g. benzoic acid, citric acid, potassium citrate, lithium citrate, potassium acetate, sodium acetate, salicylic acid, sodium salicylate, methyl salicylate, glycol salicylate, tartaric acid, potassium tartrate, sodium tartrate, lactic acid, quinine sulfate, cinchonine sulfate, strychnine sulfate, morphine sulfate, morphine acetate, quinine tartrate, tannic acid, morphine hydrochloride, boric acid, lauryl sulfate tri-ethanol amine, stearyl chloride trimethyl ammonium, benzalkonium chloride, benzethonium chloride, thioglycolic acid, sodium thioglycolate, etc. are referred to, however, they are not the limited examples.

As to the oxidizing agents, hydrogen peroxide solution, sodium-, potassium- or calcium-perchlorate, sodium-, potassium- or calcium-hypochlorite, stabilized chlorine dioxide, potassium- or sodium-bromate, sodium- or potassium-perborate, etc. are cited.

As to the polar media to dissolve or disperse these, media with high hydrogen bonding such as water, alcohols such as methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, ketones such as acetone, methyl ethyl ketone, glycols such as ethylene glycol, propylene glycol, dipropylene glycol, ethers such as diglyme, tetraglyme, propylene glycol mono-methyl ether, di-ethylene glycol mono-methyl ether, etc. alone or mixtures of these are referred to. And further, non-polar media such as hydrocarbons (e.g. nitromethane, toluene, cyclohexane, kerosene, iso-paraffin, etc.) or halogenated hydrocarbons (e.g. 1,1,1-trichloroethane, methylene chloride, carbon tetrachloride, dichloropentane, etc.) can be used in the form of mixtures with the polar media.

The present invention is also related to the aerosol articles of the aerosol cans, the inner wall of which is coated with the aforementioned PVdF-film, filled with spraying agents and polar medium mixtures of polar media, dissolving or dispersing these acids and/or compounds possibly generating acids, and at least one oxidizing agent.

As to the spraying agents, compounds having at least one or more hydrogen atom in the molecule are suitable. Concretely, methyl chloride, dichloromonofluoromethane (Freon 21), monochlorodifluoromethane (Freon 22), dichlorotrifluoroethane (Freon 123), monochlorotetrafluoroethane (Freon 124), dichlorodifluoroethane (Freon 132), monochlorodifluoroethane (Freon 142b), difluoroethane (Freon 152), dimethyl ether, propane, butane, isobutane, etc. can be cited. And the compounds not having hydrogen in the molecule such as trichloromonofluoromethane (Freon 11), dichlorodifluoromethane (Freon 12), trichlorotrifluoroethane (Freon 113), dichlorotetrafluoroethane (Freon 114), etc. can be used as mixtures with the aforementioned spraying agents.

The treatment of each ingredient of the undiluted solution, the formulation ratio between the undiluted solution and spraying agents, etc. may be determined suitably according to the uses.

This invention will be explained on the basis of the following examples, however, this invention is not limited to such examples.

Example 1

The inner wall of an aerosol can (the outer diameter: 50 mm, height: 130 mm) made from aluminum is treated with the surface coating as described on Table 1 and an antiphlogistic analgesic of the following recipe is filled up and equipped with an aluminum valve, inner wall of which is coated as described on Table 1, to prepare an aerosol article.

[A recipe of an antiphlogistic analgesic]:

	wt %
Methyl salicylate	3.0
Glycol salicylate	2.0
Menthol	4.0
Ethanol	27.0
Purified water	43.7
Dimethyl ether	12.0
Butane	8.3

These aerosol articles were left at 45 °C for 3 months and at the room temperature for 12 months to observe the inner wall surface status of the cans and the valves.

The results are shown on Table 1.

Further, the evaluation has been done according to the following standard.

◎: Absolutely normal.

○: Coating layer was slightly discolored, softened.

△: Blister generated in the coating layer.

X: Coating layer peeled off, corrosion generated on the base-material.

[Table 1]:

Exp-mnt No.	Kind of the coating layer		Results	
	Can inner wall	Valve inner wall	Can inner wall	Valve inner wall
1	PVdF	PVdF	◎	◎
2	PVdF	Anodic oxidation	◎	○
3	PVdF	Epoxy resin	◎	△
4	PVdF	MICOFLEX	◎	○
5	Epoxy phenol resin	PVdF	△	◎
6	Epoxy phenol resin	Anodic oxidation	△	△
7	Epoxy phenol resin	Epoxy resin	△	△
8	Epoxy phenol resin	MICOFLEX	△	△
9	Epoxy urea resin	PVdF	X	◎
10	Epoxy urea resin	Anodic oxidation	X	△
11	Epoxy urea resin	Epoxy resin	X	△
12	Epoxy urea resin	MICOFLEX	X	△
13	MICOFLEX	PVdF	△	◎
14	MICOFLEX	Anodic oxidation	△	△
15	MICOFLEX	Epoxy resin	△	△
16	MICOFLEX	MICPFLEX	△	△

Note: MICOFLEX (phonetic) is a vinyl resin.

Example 2-8

Each aerosol composition shown on the Table 2 was filled in a container, the structure of which is shown on Table 3 as an aerosol can equipped with a valve, and the status of the can inner wall and the valve inner wall was investigated.

The results were shown on Table 3:

[Table 2]:

Formulation example	Use	Composition of the aerosol formulation			
		Acid and/or compound generating acid, and oxidizing agent (wt%)	Polar medium (wt%)	Spraying agent (wt%)	Others (wt%)
2	Sunburn treatment	Dipotassium glycylrhizinate (0.1) Citric acid (0.05)	1,3-Butyleneglycol (2.5) Ethanol (5.0) Purified water (72.25)	Dimethyl ether (20.0)	Diphenhydramine (0.1)
3	Hair treatment mousse	Alkyl chloride trimethyl ammonium (1.8) Lauric acid diethanol amid (0.18) p-Hydrxybenzoic acid ester (0.09) Vinylpyrrolidone-N,N-dimethyl-aminoethyl methacrylic acid copolymer diethyl sulfate (4.6)	Ethanol (9.2) Propylene glycol (4.6) Purified water (89.54)	Dimethyl ether (1.8) Propane (1.8) Butane (5.4)	Surfactant (0.91) Cetanol (0.18)
4	Depilatory agent (mousse-type)	Thioglycolic acid (2.7) Citric acid (0.13)	Propylene glycol (4.5) Purified water (75.99)	Dichlorodifluoro methane (7.0) Dichlorotetrafluor oethane (3.0)	Surfactant (2.7) Cetanol (0.45) Squalane (0.9) Sidium hydroxide (2.57) Calcium hydroxide (0.06)
5	Medicine for athlete's foot	Maleic acid chloro-phenyl-amine (0.6)	Ethanol (3.3) Purified water (12.8)	Dichlorotetrafluor oethane (80)	Tolnaftate (0.4) Thianthol (2.6) Surfactant (0.3)
6	Disinfectant deodorant	Benzalkonium chloride (0.2)	Purified water (0.05) Ethanol (4.9) Isopropyl alcohol (4.8)	Dichlorodifluoro methane (45) Butane (45)	Plant extracts (0.05)
7	Hair spray	Octyl dodecyl myristate (0.2) p-Hydroxybenzoic acid ester (0.04) Alkyltrimethylammonium chloride (0.05) Vinylpyrrolidone-N-ethyl-N,N-dimethyl-N-ethylmethacryloyl ammonium sulfate copolymer (0.05)	Ethanol (34.6)	Monochlorodifluo romethane (25.5) Dichloromonofluo romethane (39.5)	
8	Insect repellent		Ethanol (33.4) Purified water (22.3)	Dichlorodifluoro methane (7.6) Dichlorotetrafluor omethane (7.6) Dimethyl ether	Deet (6.3)

[Table 3]:

Example	Formulation example	Container				Test results	
		Can		Valve			
		Material	Internal coating layer	Material	Internal coating layer	Inner can	Inner valve
2-1	2	Aluminum	PVdF	Aluminum	PVdF	◎	◎
2-2		Aluminum	Epoxy phenol resin	Aluminum	Epoxy resin	X	X
2-3		Aluminum	MICOFLEX	Aluminum	MICOFLEX	△	△
3-1	3	Aluminum	PVdF	Aluminum	PVdF	◎	◎
3-2		Aluminum	Epoxy phenol resin	Aluminum	Epoxy resin	△	△
4-1	4	Blik	PVdF	Blik	PVdF	◎	◎
4-2		Blik	PVdF	Blik	Stainless steel 304	◎	Some corrosion
4-3		Blik	Epoxy phenol resin	Blik	Epoxy resin	X	X
5-1	5	Aluminum	PVdF	Aluminum	PVdF	◎	◎
5-2		Aluminum	Epoxy phenol resin	Aluminum	Epoxy resin	X	X
5-3		Aluminum	MICOFLEX	Aluminum	MICOFLEX	△	△
6-1	6	Blik	PVdF	Blik	PVdF	◎	◎
6-2		Blik	Epoxy phenol resin	Blik	Epoxy phenol resin	X	X
7-1	7	Aluminum	PVdF	Aluminum	PVdF	◎	◎
7-2		Aluminum	Epoxy phenol resin	Aluminum	Epoxy phenol resin	△	△
8-1	8	Aluminum	PVdF	Aluminum	PVdF	◎	◎
8-2		Aluminum	Epoxy phenol resin	Aluminum	Epoxy phenol resin	△	△
8-3		Aluminum	MICOFLEX	Aluminum	MICOFLEX	△	○

[The effect of the invention]

According to the present invention, aerosol cans showing much better resistance against compounds, so far difficult to be used for aerosol products, can be offered, thus the aerosol articles with a wider effectiveness than before can be proposed.

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